Abstract: The light pnictine oxides $R_3NO$, $R_3PO$, and $R_3AsO$ comprise a well-characterized class of monomeric molecules with a tetrahedral geometry about the pnictogen center. In contrast, the preparation of the corresponding Sb and Bi species has long proved challenging. For the heavier pnictogens, reduced orbital overlap with oxygen increases charge separation, which in turn increases the electrophilicity of the pnictogen and the nucleophilicity of the oxygen. Furthermore, the heavier pnictogens have an increased propensity to expand their coordination spheres. Consequently, stibine oxides and bismuthine oxides occur as oligomeric/polymeric materials. We have recently employed a kinetic stabilization strategy to isolate the first example of an unperturbed monomeric stibine oxide. We have examined the electronic structure of the newly isolated stiboryl functional group using a variety of physical and theoretical techniques. These investigations have guided our exploration of the reactivity of this previously inaccessible unsaturated (heavy pnictogen–oxygen bond).